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A New Synthetic Approach to *N*-Arylquinolino[2,3,4-*at*]porphyrins from *β*-Arylaminoporphyrins

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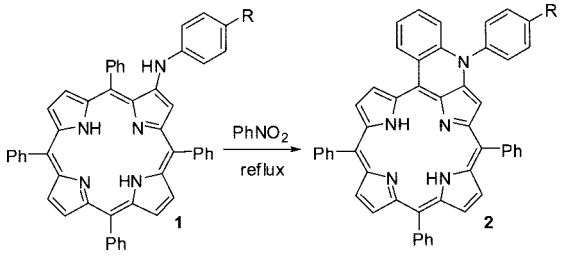

A new reaction leading to porphyrins bearing fused rings is described. Novel *N*-arylquinolino[2,3,4-*at*]porphyrins **2** were obtained by thermal oxidative cyclization of *β*-arylaminoporphyrins **1**. The starting *β*-arylaminoporphyrins were prepared by two routes: (i) nucleophilic displacement of the nitro group from 2-nitro-5,10,15,20-tetraphenylporphyrin by anilines and (ii) palladium-catalyzed amination of bromobenzene derivatives with (2-amino-5,10,15,20-tetraphenylporphyrinato)nickel(II). The *N*-arylquinolino[2,3,4-*at*]porphyrins show interesting UV−vis spectra with strong absorption bands in the red region.

The chemical and physical properties displayed by porphyrins render them appealing compounds for several applications. Medicine, chemistry and physics are widely explored areas where these compounds have shown promising applications, namely as agents for cancer photodynamic therapy, as catalysts, and as novel functional materials.[1]

The transformation of readily available *meso*-tetraarylporphyrins into new compounds exhibiting adequate features for a required application has been the goal of several research groups. 2-Nitroporphyrins[2] have been extensively used as starting materials for the synthesis of other porphyrin derivatives, namely by direct nucleophilic substitution of the 2-nitro group by thiolates,[3] alkoxides,[4,5] Grignard or organolithium reagents,[6] 1,3-dicarbonyl compounds,[7] azide ion,[8] etc. The conversion of the nitro group into amino and diazonium groups, along with their subsequent reactions, represents another important synthetic tool for porphyrin derivatization.[9–13]

Here we report the synthesis of 2-arylaminoporphyrins **1** and their subsequent conversion into novel *N*-arylquinolino[2,3,4-*at*]porphyrins **2**. This is a new reaction leading to porphyrins bearing fused rings.[14] Compounds **2** are structurally related with the ones obtained by treatment of (2-nitro-5,10,15,20-tetraphenylporphyrinato)nickel(II) with triethyl phosphite[15] or by thermal cyclization of (2-azido-5,10,15,20-tetraphenylporphyrinato)nickel(II).[16]

Two different approaches were used to prepare the 2-arylaminoporphyrins **1**: (a) by nucleophilic substitution of the nitro group of 2-nitro-5,10,15,20-tetraphenylporphyrin (2-NO_2-TPP) by anilines (Scheme 1) and (b) by palladium-catalyzed amination reactions of (2-amino-5,10,15,20-tetraphenylporphyrinato)nickel(II) with bromobenzene derivatives (Scheme 2).

Our studies involving the direct displacement of the nitro group in 2-NO_2-TPP were initiated by refluxing the porphyrin in aniline under a nitrogen atmosphere. After 20 h, the TLC of the reaction mixture showed the complete conversion of the starting porphyrin into one major product and two minor ones. After the workup, the reaction products were purified by column chromatography and preparative TLC. The major compound was identified (vide infra) as the 2-phenylaminoporphyrin **1a** (53% yield), and the other two products were identified as the unexpected *N*-phenylquinolino[2,3,4-*at*]porphyrin **2a** (6% yield) and chlorin **3** (22% yield). Compound **1a** and the corresponding copper and zinc complexes have already been reported.[6,17,18]

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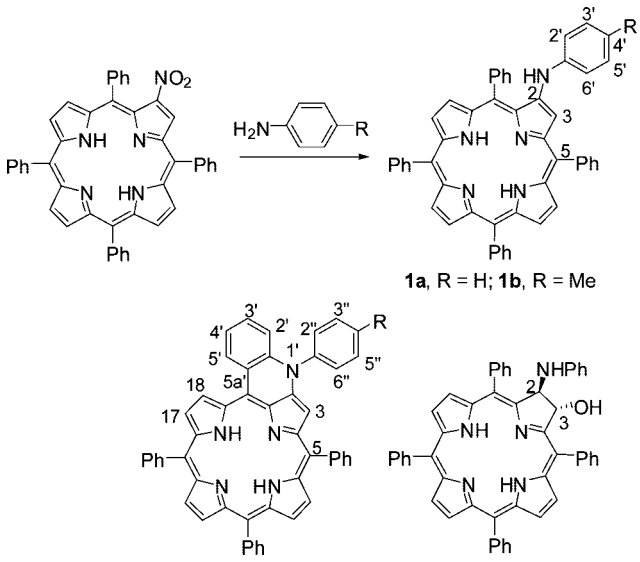
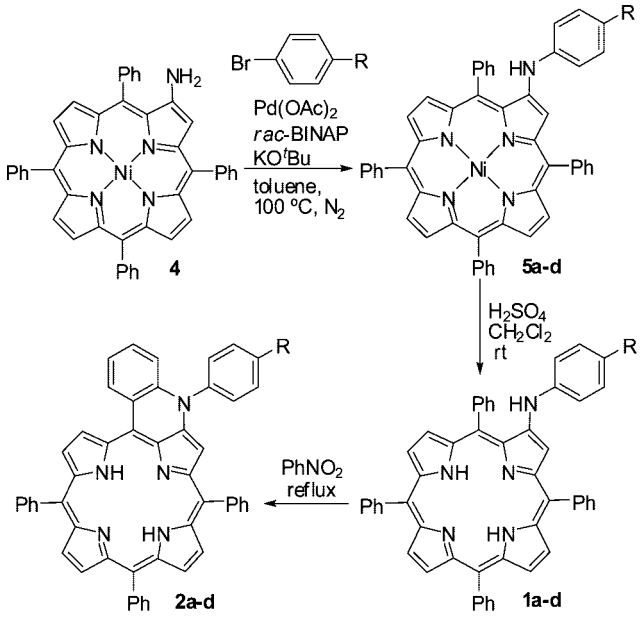
SCHEME 1. Synthesis of *N*-Arylaminoporphyrins 1



SCHEME 2. Synthesis of *N*-Arylquinolinoporphyrins 2a−d via Palladium-Catalyzed Amination Followed by Thermal Oxidative Cyclization



Preliminary attempts to perform the reaction between 2-NO_2-TPP and *p*-toluidine (72 h at 180 °C and in the absence of solvent) did not lead to the expected products. However, when this reaction was conducted in refluxing *o*-dichlorobenzene (48 h), compound **1b** was obtained in 32% yield, compound **2b** was formed in trace amounts, and no chlorin derivative of type **3** was detected.

When the reaction of 2-NO_2-TPP with aniline was performed in refluxing *o*-dichlorobenzene, compounds **1a**, **2a**, and **3** were again obtained but in a different product yield distribution: 19% yield, 26% yield, and trace amounts, respectively.

Since the formation of compounds **2** involves the oxidative cyclization of **1**, we decided to study the cyclization of **1a** in refluxing nitrobenzene.[19] After **1a** was refluxed in nitrobenzene for 30 h, the TLC of the reaction mixture showed its complete conversion into **2a**. Purification by column chromatography afforded **2a** in 87% yield. Similarly, heating **1b** in refluxing nitrobenzene afforded **2b** in 81% yield. These results clearly show that compounds **2** result from the oxidative cyclization of the arylaminoporphyrins **1**.

In order to study the effect of electron-withdrawing groups in the oxidative cyclization of the arylaminoporphyrins **1**, we decided to prepare compounds **1c** and **1d**, but the reaction of 2-NO_2-TPP with *p*-chloroaniline and *p*-bromoaniline, in *o*-dichlorobenzene, did not lead to the required products. Therefore, we converted 2-NO_2-TPP into the corresponding 2-amino derivative **4** and used it to prepare the corresponding 2-arylaminoporphyrins **5** via the palladium-catalyzed amination methodology (Scheme 2).[17,18,20,21] The reaction between **4** and the commercially available *p*-bromochlorobenzene and *p*-dibromobenzene under palladium-catalyzed conditions afforded, respectively, compounds **5c** (68% yield) and **5d** (43% yield). This methodology was also extended to the reaction of **4** with bromobenzene and *p*-bromotoluene affording the expected products **5a** (69% yield) and **5b** (78% yield), which are the corresponding nickel complexes of the arylaminoporphyrins **1a** and **1b**.

As indicated in Scheme 2, the amination reactions were performed in toluene at 100 °C, under a nitrogen atmosphere, using $Pd(OAc)_2$ as catalyst, *rac*-BINAP as ligand, and KO^{t}Bu as the base. The reactions were ended after the conversion of the starting porphyrin **4** into a main product with higher R_f (monitored by TLC). After workup, the major product was isolated by preparative TLC and identified as **5** by spectroscopic data. No *N*-arylquinolinoporphyrins or hydroxychlorins were formed in these reactions. Demetalation of compounds **5a−d** with 10% sulfuric acid in dichloromethane afforded the corresponding free-bases **1a−d** in ca. 70% yield.

Compounds **2c** and **2d** were obtained in 75% and 76% yield, respectively, by refluxing nitrobenzene solutions of **1c** and **1d** for 30 h followed by purification by column chromatography. It is worth mentioning that the nickel derivatives **5** also led to the expected *N*-arylquinolino products when heated in refluxing nitrobenzene.

The structural elucidation of the new compounds involved the use of several NMR techniques (^{1}H, ^{13}C, COSY, HSQC, HMBC, and NOESY), HRMS, and UV−vis. In addition, the structure of compound **2a** was unequivocally confirmed by single-crystal X-ray diffraction studies (Figure 1).[22]

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(22) Crystal data: $C_{50}H_{33}N_5$, $M = 703.81$, $T = 150(2)$ K, monoclinic, space group $P21/n$, $Z = 4$, $a = 17.7092(7)$ Å, $b = 10.6971(3)$ Å, $c = 19.5954(7)$ Å, $\alpha = 104.6350(10)°$, $V = 3591.7(2)$ Å^3, brown prism with crystal size of 0.20 × 0.08 × 0.04 mm^3. Of a total of 77784 reflections collected; 6113 were independent ($R_{int} = 0.0819$). Final R1 = 0.0455 [$I > 2\sigma(I)$] and wR2 = 0.1151 (all data). CCDC 642548. See the Supporting Information for further details on the crystal solution and refinement.

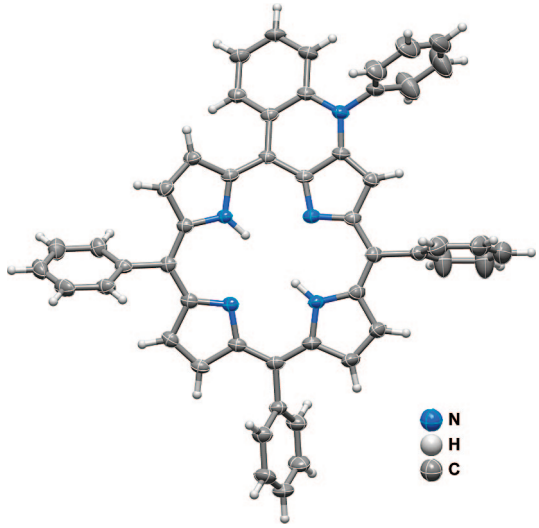

FIGURE 1. Molecular unit of **2a**. Non-hydrogen atoms are represented as thermal ellipsoids drawn at the 50% level.

The ^{1}H NMR spectra of all the arylaminoporphyrin derivatives (**1a**−**d** and **5a**−**d**) are consistent with β-substituted porphyrins showing the resonance corresponding to H-3 as a singlet (or under a multiplet) at ca. δ 8.2 ppm.

The ^{1}H NMR spectra of the *N*-arylquinolino[2,3,4-*at*]porphyrins **2a**−**d** show interesting features, with the signals of protons H-18 and H-5′ appearing at low field (δ ~9.7 ppm). In compound **2a**, for instance, the resonances of these protons emerge as two doublets at δ 9.67 ppm (J = 4.5 Hz) and 9.68 ppm (J = 7.0 Hz), respectively. The COSY and NOESY spectra of **2a** clearly indicate that the signal at δ 9.67 ppm (H-18) correlates with the resonance of H-17 (δ 8.82 ppm) and the signal at δ 9.68 ppm (H-5′) correlates with the resonance of H-4′ (included in the multiplet at δ 7.64−7.90 ppm). The same pattern is also observed in the spectra of compounds **2b**−**d**.

The UV−vis spectrum of **3** is typical of chlorins showing a strong Q absorption band at 642 nm (log ε = 4.4). The mass spectrum shows a peak at *m*/*z* 724 [(M + H)$^+$], differing from **1a** in 18 mass units, which is consistent with the addition of one water molecule. Its ^{1}H NMR spectrum shows the signals corresponding to the resonance of six β-pyrrolic protons (δ 8.3−8.7 ppm), indicative of a disubstituted derivative, and also the characteristic signals corresponding to resonance of the aniline protons. The spectrum also shows three signals at δ −1.88, 2.46, and 3.90 ppm which disappear when D_2O is added to the sample, thus being assigned to the resonances of the inner N*H*, O*H* and β-N*H* protons. The HMBC spectrum shows ^{3}J correlation between the doublet at δ 3.90 ppm (J = 4.8 Hz) and C-2′,6′ (δ 113.0 ppm), allowing its assignment to the resonance of the β-N*H* proton. The broad singlet at δ 2.46 ppm can be, therefore, assigned to the resonance of the O*H* proton. In the COSY spectrum, the β-N*H* signal (δ 3.90 ppm) correlates with the doublet at δ 5.90 ppm (J = 4.8 Hz) which corresponds to the resonance of H-2 proton, being the singlet at δ 6.21 ppm assigned to the H-3 resonance. The same spectrum shows that protons H-2 and H-3 do not correlate with each other, denoting a trans configuration with a dihedral angle around 90°.

The UV−vis spectra of compounds **1a**, **2a**, and **3** (shown as examples of the three structural types of compounds described in this paper) are depicted in Figure 2. The most interesting

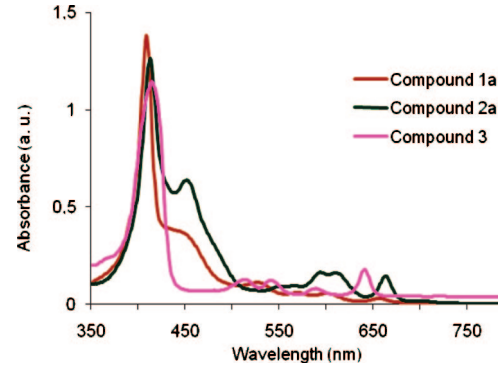

FIGURE 2. Visible absorption spectra of compounds **1a**, **2a**, and **3** in dichloromethane.

spectra are those from the *N*-arylquinolino[2,3,4-*at*]porphyrins **2** which show intense absorption bands at $\lambda \approx$ 590−610 and 660 nm.

In conclusion, two new methodologies were developed for the synthesis of the novel *N*-arylquinolino[2,3,4-*at*]porphyrins **2**. The first one involves the reaction of 2-NO_2-TPP with aniline or *p*-toluidine. These reactions afford mixtures of the corresponding 2-arylaminoporphyrin derivatives **1** and *N*-arylquinolino[2,3,4-*at*]porphyrins **2** (and the hydroxychlorin **3** in the case of the reaction with aniline). The second approach involves the formation of 2-arylaminoporphyrins via palladium-catalyzed reactions of (2-amino-5,10,15,20-tetraphenylporphyrinato)nickel(II) **4** with bromobenzene derivatives. After demetalation to **1a**−**d**, these derivatives are easily converted into derivatives **2** by oxidative cyclization in refluxing nitrobenzene.

Compounds **2** show interesting UV−vis spectra with intense absorption bands in the red region of the visible spectrum, which make them potential candidates for application in various scientific areas.

Experimental Section

Synthesis of *N*-Arylquinolino[2,3,4-*at*]porphyrins 2 from Arylaminoporphyrins 1. A stirred solution of each **1a**−**d** (ca. 20 mg) in nitrobenzene (2 mL) was kept under reflux for 30 h. The reaction mixture was poured on top of a silica gel chromatography colum, and the nitrobenzene was eluted with light petroleum. The reaction products were then eluted using a 1:1 mixture of dichloromethane and light petroleum. Compounds **2a**−**d** were obtained as dark solids, after precipitation from dichloromethane and hexane, with 87% (17.2 mg), 81% (16.1 mg), 75% (14.9 mg), and 76% (15.1 mg) yields, respectively.

Data for *N*-phenylquinolino[2,3,4-*at*]porphyrin, 2a: mp 230−232 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ −1.25 (s, 2H, N*H*), 7.64−7.90 (m, 18H, H-3, H-2′,3′,4′, H-*m*,*p*-Ph-5,10,15 and N-C_6H_5), 8.10−8.11, 8.16−8.18 and 8.26−8.28 (3m, 6H, H-*o*-Ph-5,10,15), 8.59 (d, J = 4.8 Hz, 1H, H-β), 8.67−8.68 (m, 2H, H-12,13), 8.74 (d, J = 4.8 Hz, 1H, H-β), 8.82 (d, J = 4.5 Hz, 1H, H-17), 9.67 (d, J = 4.5 Hz, 1H, H-18), 9.68 (d, J = 7.0 Hz, 1H, H-5′); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 101.3 (C-3); 110.4; 115.5 (C-2′); 116.5, 117.3; 121.9 or 122.0 (C-4′); 123.3; 124.0 (C-18); 126.5 (C-17); 126.7, 126.8, 127.1, 127.37, 127.41, 127.5, 127.7, 129.1, 129.3, 130.9 (C-*m*,*p*-Ph-5,10,15 and C-3′); 128.6, 132.3 and 134.54 (C-β); 134.0, 134.47 and 134.7 (C-*o*-Ph-5,10,15); 135.0 (C-5′); 136.3, 141.3, 142.2, 142.4, 145.9, 155.3. UV−vis (CH_2Cl_2) λ_{max} (log ε) 412 (5.2), 451 (4.9), 594 (4.3), 610 (4.3), 663 (4.2); HRMS (ESI) calcd for $C_{50}H_{34}N_5$ (M + H)$^+$ 704.2794, found 704.2809.

Data for *N*-(*p*-methylphenyl)quinolino[2,3,4-*at*]porphyrin, 2b: mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ −1.22 (s, 2H, N*H*), 2.64 (s, 3H, CH_3), 7.62 (d, J = 8.0 Hz, 1H, H-2′), 7.66−7.88

(m, 16H, H-3, H-3′,4′, H-*m*,*p*-Ph-5,10,15 and N-C_6H_4Me), 8.10−8.13, 8.16−8.18 and 8.26−8.28 (3m, 6H, H-*o*-Ph-5,10,15), 8.59 (d, J = 4.5 Hz, 1H, H-β), 8.66−8.69 (m, 2H, H-12, 13), 8.74 (d, J = 4.5 Hz, 1H, H-β), 8.81 (d, J = 4.8 Hz, 1H, H-17), 9.66 (d, J = 4.8 Hz, 1H, H-18), 9.67 (d, J = 8.0 Hz, 1H, H-5′); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 21.6 (CH_3); 101.2 (C-3); 115.6 (C-2′); 121.9 (C-4′); 123.3; 124.1 (C-18); 126.7 (C-17); 126.8, 127.1, 127.3, 127.7 (C-*m*,*p*-Ph-5,10,15); 128.7 (C-2″,6″); 131.5 (C-3″,5″); 126.5, 128.6, 132.2 and 134.54 (C-β); 134.0, 134.47 and 134.7 (C-*o*-Ph-5,10,15); 135.0 (C-5′); 138.7, 139.0, 142.3, 142.4, 145.4, 149.0; UV−vis (CH_2Cl_2) λ_{max} (log ε) 413 (5.2), 452 (4.9), 595 (4.3), 611 (4.3), 663 (4.2); HRMS (ESI) calcd for $C_{51}H_{36}N_5$ $(M + H)^+$ 718.2965, found 718.2946.

Data for *N*-(*p*-chlorophenyl)quinolino[2,3,4-*at*]porphyrin, 2c: mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ −1.33 (s, 2H, N*H*), 7.62 (d, J = 8.0 Hz, 1H, H-2′), 7.68−7.86 (m, 16H, H-3, H-3′,4′, H-*m*,*p*-Ph-5,10,15 and N-C_6H_4Cl), 8.10−8.12, 8.16−8.18 and 8.26−8.28 (3m, 6H, H-*o*-Ph-5,10,15), 8.61 (d, J = 4.5 Hz, 1H, H-β), 8.68−8.70 (m, 2H, H-12, 13), 8.76 (d, J = 4.5 Hz, 1H, H-β), 8.83 (d, J = 4.8 Hz, 1H, H-17), 9.66 (d, J = 8.5 Hz, 1H, H-5′), 9.68 (d, J = 4.8 Hz, 1H, H-18); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ 101.3 (C-3); 110.2; 115.2 (C-2′); 116.7, 117.3, 117.8; 122.09 or 122.15 (C-4′); 123.3, 123.5, 124.0; 124.1 (C-18); 126.5 (C-17); 126.7, 126.78, 126.84, 127.2, 127.3, 127.4, 127.6, 127.7 and 127.8 (C-*m*,*p*-Ph-5,10,15); 130.7 and 131.3 (C-2″,3″,5″,6″); 128.57, 128.64, 128.7, 132.51, 132.53 and 134.7 (C-β); 133.9, 134.5, 134.6 and 134.7 (C-*o*-Ph-5,10,15); 135.2 (C-5′); 140.3, 142.2, 142.35, 142.37, 145.5; UV−vis (CH_2Cl_2) λ_{max} (log ε) 412 (4.7), 449 (4.5), 592 (3.8), 609 (3.8), 662 (3.8); HRMS (ESI) calcd for $C_{50}H_{33}ClN_5$ $(M + H)^+$ 738.2419, found 738.2438.

Data for *N*-(*p*-bromophenyl)quinolino[2,3,4-*at*]porphyrin, 2d: mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ −1.33 (s, 2H, N*H*), 7.60 (d, J = 8.4 Hz, 1H, H-2′), 7.69−7.98 (m, 16H, H-3, H-3′,4′, H-*m*,*p*-Ph-5,10,15 and N-C_6H_4Br), 8.09−8.12, 8.15−8.19 and 8.25−8.28 (3m, 6H, H-*o*-Ph-5,10,15), 8.60 (d, J = 4.7 Hz, 1H, H-β), 8.68−8.70 (m, 2H, H-12,13), 8.76 (d, J = 4.7 Hz, 1H, H-β), 8.83 (d, J = 4.7 Hz, 1H, H-17), 9.66 (d, J = 7.5 Hz, 1H, H-5′), 9.67 (d, J = 4.7 Hz, 1H, H-18); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 101.3 (C-3); 110.2; 115.2 (C-2′); 116.7, 117.3; 122.1 or 122.2 (C-4′); 123.2, 123.3; 124.1 (C-18); 126.5 (C-17); 126.7, 126.77, 126.83, 127.2, 127.4, 127.6, 127.8 (C-*m*,*p*-Ph-5,10,15); 131.0 (C-2″,3″,5″,6″); 128.57, 128.63, 132.5 and 134.6 (C-β); 134.3; 133.9, 134.5 and 134.7 (C-*o*-Ph-5,10,15,20); 135.2 (C-5′); 136.1, 140.3, 142.2, 142.33, 142.35, 145.6; UV−vis (CH_2Cl_2) λ_{max} (log ε) 412 (4.8), 449 (4.5), 592 (3.9), 609 (3.9), 662 (3.9); HRMS (ESI) calcd for $C_{50}H_{33}BrN_5$ $(M + H)^+$ 784.1905, found 784.1901.

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Supporting Information Available: Experimental procedures and full spectroscopic data for all new compounds. Details on the data collection, crystal solution, and refinement for porphyrin **2a**. Additional structural drawings of **2a**. Crystal structure (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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